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Reactions of Imidoyl Isoselenocyanates with Aromatic 2-Amino N-Heterocycles and 1-Methyl-1H-imidazole

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Abstract: The reaction of N-phenylimidoyl isoselenocyanates 1 with 2-amino-1,3-thiazoles 10 in acetone proceeded smoothly at room temperature to give 4H-1,3-thiazolo[3,2-a] [1,3,5]triazine-4-selones 13 in fair yields (Scheme 2). Under the same conditions, 1 and 2-amino-3-methylpyridine (11) underwent an addition reaction, followed by a spontaneous oxidation, to yield the 3H-4l4-[1,2,4]selenadiazolo[1',5':1,5] [1,2,4]selenadiazolo[2,3-a]pyridine 14 (Scheme 3). The structure of 14 was established by X-ray crystallography (Fig. 1). Finally, the reaction of 1-methyl-1H-imidazole (12) and 1 led to 3-methyl-1-(N-phenylbenzimidoyl)-1H-imidazolium selenocyanates 15 (Scheme 4). In all three cases, an initially formed selenourea derivative is proposed as an intermediate.

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Reactions of Imido-yl Isoselenocyanates with Aromatic 2-Amino- *N*-heterocycles and 1-Methylimidazole

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The reaction of *N*-phenylimidoyl isoselenocyanates **1** with 2-amino-1,3-thiazoles **10** in acetone proceeded smoothly at room temperature to give 4*H*-1,3-thiazolo[3,2-*a*][1,3,5]triazine-4-selones **13** in fair yields (*Scheme 2*). Under the same conditions, **1** and 2-amino-3-methylpyridine (**11**) underwent an addition reaction followed by a spontaneous oxidation to yield the 3*H*-4 λ^4 -[1,2,4]selenadiazolo[1',5':1,5][1,2,4]selenadiazolo[2,3-*a*]pyridine **14** (*Scheme 3*). The structure of the latter was established by X-ray crystallography (*Figure*). Finally, the reaction of 1-methylimidazole (**12**) and **1** led to 1-methyl-3-(*N*-phenylbenzimidoyl)imidazolium selenocyanates **15** (*Scheme 4*). In all three cases, an initially formed selenourea derivative is proposed as an intermediate.

Introduction. – The interest in selenium-containing organic compounds is unbroken, mainly because of their biological activities [1][2]. For this reason, convenient syntheses of selenaheterocycles and heterocyclic selones are much sought after. In recent years, the use of isoselenocyanates as easily accessible and safe building blocks has been demonstrated successfully [3]. Among them, the imidoyl derivatives of type **1**, which can be prepared conveniently from *N*-phenylimidoyl chlorides and potassium selenocyanate [4][5] are of special interest because of their bifunctional nature.

We have shown that the reaction of **1** with primary or secondary amines leads to selenourea derivatives, which by subsequent reaction with activated bromomethylene compounds and treatment with a strong base yield 2-amino-1,3-selenazoles **2** [5] (*Scheme 1*). Imidoyl isoselenocyanates **1** with $R^1 = 2\text{-(chloromethyl)phenyl}$ react with amines to give 6*H*-5,1,3-benzoselenadiazocines **3** [6]. In both cases, the initial reaction is a nucleophilic attack of the amine onto the isoselenocyanate, followed by an addition of the intermediate thiourea derivative with an electrophile in an inter- or intramolecular fashion. With amidines **4** and **6**, respectively, 1,3,5-triazineselones **5** and **7** are formed smoothly at room temperature [7] (*Scheme 1*). Similarly, 2-amino-4,5-dihydro-1,3-thiazole (**8**) reacts with **1** to give the fused triazineselones **9**. The formation of the triazineselones **5**, **7**, and **9** has been rationalized by the initial formation of a selenourea derivative, followed by cyclization and elimination of aniline ($Ar^2 = Ph$).

Scheme 1

The goal of the present study was the extension of the reaction of **1** with amidines to aromatic 2-aminoazaheterocycles, such as 2-amino-1,3-thiazoles **10** and 2-aminopyridines **11**, *i.e.*, aromatic heterocycles with a formal amidine group, as well as to 1-methylimidazole (**12**).

Results and Discussion. – The starting materials, *i.e.*, *N*-phenylbenzimidoyl isoselenocyanates **1a** – **1c** were prepared as described in [5]. In acetone at room temperature, they underwent a smooth reaction with equimolar amounts of 2-amino-1,3-thiazoles **10a** and **10b**, respectively, to give 4*H*-1,3-thiazolo[3,2-*a*][1,3,5-triazine-4-selones **13** in 53 – 63% yield (*Scheme 2*, *Table 1*). The products precipitated directly from the reaction mixture as orange-yellow solids. Their structure was derived from the spectroscopic data, the elemental analyses, and by analogy to the earlier described 6,7-dihydro derivative **9** ($\text{Ar}^1 = 4\text{-ClC}_6\text{H}_4$), the structure of which has been established by X-ray crystallography [7]²⁾. The formation of **13** can be rationalized as shown in *Scheme 2*: nucleophilic addition of the ring N-atom of **10** to the isoselenocyanate **1** leads to the intermediate selenourea derivative **B**, which spontaneously undergoes cyclization to give the fused ring system **C**. Elimination of aniline from the latter yields the product **13**.

Scheme 2

Table 1. Prepared 2-Aryl-4*H*-1,3-thiazolo[3,2-*a*][1,3,5]triazine-4-selones **13**

The next experiment was carried out with 2-amino-3-methylpyridine (**11**) and **1c**. It is worth mentioning that the reaction in acetone also occurred at room temperature. After

²⁾ The analogous reaction of phenylbenzimidoyl isothiocyanate with **10a** has been described by *Barnikov* and *Ebeling* [8]. Furthermore, 2-aryl-4*H*-1,3-thiazolo[3,2-*a*][1,3,5]triazine-4-thiones have been obtained in the reaction of **10a** with aroyl isothiocyanates, which were prepared *in situ* from aroyl chlorides and NH_4SCN [9]. On the other hand, **10a** and alkoxycarbonyl isothiocyanates reacted in a non-selective manner *via* nucleophilic addition of either the NH_2 group or the ring N-atom [10].

stirring for 3 h, the mixture was poured into H₂O leading to a yellowish, crystalline product in *ca.* 65% yield. The NMR spectra indicated clearly that no aniline was eliminated, and also the elemental analyses were in accordance with a 1:1 adduct. Therefore, the structure of the selenourea derivative **D** was proposed (*Scheme 3*). Surprisingly, the ¹H-NMR spectrum as well as the CI-MS (NH₃) showed that two H-atoms were missing. For this reason, a crystal-structure determination of the product was undertaken confirming that 2-(4-chlorophenyl)-9-methyl-3-phenyl-3*H*-4λ⁴-[1,2,4]selenadiazolo[1',5':1,5][1,2,4]selenadiazolo[2,3-*a*]pyridine (**14**) was formed (*Fig. 1*).

Scheme 3

Fig. 1. *ORTEP* plot [11] of the molecular structure of **14** (50% probability ellipsoids, arbitrary numbering of the atoms)

The Se-atom appears to be three-coordinated in that it receives two dative bonds, one from the N-atom of the pyridine ring and the other from the N-atom adjacent to the unsubstituted Ph group. These N–Se bonds are asymmetric, differing by about 0.12 Å, and they are 0.08-0.20 Å longer than the C–Se bond. A normal N–Se single bond is about 1.85 Å, which is in the range of 0.15-0.27 Å shorter than the N–Se bonds seen here. The C–Se bond (1.918(2) Å) is about 0.10 Å longer than the C=Se double bond found in an analog of **13c** [7], which is consistent with the effect induced by the N–Se interactions and is indicative of partial delocalisation of the electron density in this bond. Similar C–Se bond lengths of about 1.90 Å have been observed in some related structures [12], where a formal C–Se single bond is adjacent to a π-system. The dative bonds complete two fused five-membered rings. The bond lengths around these rings show considerable delocalisation of all C–N bonds and the

C–Se bond, which probably implies the existence of canonical forms of a resonance structure. None of the N-atoms in the structure are protonated, which is consistent with the NMR spectra.

The two five-membered rings are quite planar with the maximum deviation from the mean plane being 0.053(2) Å for C(7). This plane is nearly coplanar with that of the fused six-membered ring, the angle between the planes being only 5.09(9)°. If the three fused rings are considered together, the maximum deviation from the mean plane is 0.095(2) Å for N(2). The planes of the chlorophenyl ring and the remaining phenyl ring make angles of 18.8(1)° and 75.39(9)°, respectively, with the mean plane of the two fused five-membered rings.

The unexpected formation of **14** may be explained by the initial addition of the amino N-atom of **11** onto the isoselenocyanate yielding the intermediate selenourea **D**. A spontaneous oxidation leads then to the isolated product. In contrast to the reactions with **10**, in which the ring N-atom was the most nucleophilic center, the NH₂ group of **11** acted as nucleophile. This observation may be rationalized by the higher aromaticity of the pyridine ring compared with that of the 1,3-thiazole ring.

Finally, 1-methylimidazole (**12**), with a formal amidine structure integrated in the five-membered ring, was reacted with **1b** and **1c**, respectively, in acetone. The reaction also proceeded at room temperature. After stirring the mixture overnight, it was poured into H₂O, and the formed precipitate was recrystallized from AcOEt. The elemental analyses showed that the molecular formulae of the products **15b** and **15c** correspond with the sum of the respective starting materials, *i.e.*, no elimination of aniline occurred. The NMR spectra also indicated clearly the presence of all expected H- and C-atoms, *e.g.* in the case of **15b**, two signals for Me groups appeared at 4.19/37.7 and 2.36/21.5 ppm. Most remarkable was a *singlet* for one H-atom at 9.30 ppm attached to C(2) of the imidazole ring (136.9 ppm).

Furthermore, the most dominant absorption band in the IR spectrum (KBr) appeared at 2061 cm^{-1} . On the basis of extended NMR investigations (HSQC, $^1\text{H}/^{13}\text{C}$ and $^1\text{H}/^{15}\text{N}$ HMBC, TOCSY, and NOESY), the structures of 1-methyl-3-(*N*-phenylbenzimidoyl)imidazolium selenocyanates **15b** and **15c** were proposed (*Scheme 4*).

Scheme 4

The three N-atoms of the 3-(benzimidoyl)imidazolium moiety of **15c** were undoubtedly localized at -202.4 (N(1)), -177.1 (N(3)), and -72.9 ppm (C=N) (*Fig. 2*). They showed the expected HMBC correlations with the H-atoms of the imidazolium ring as well as the *ortho*-H-atoms of the Ph ring. *E.g.*, N(1) shows correlations with H-C(2) at 9.35 ppm, H-C(4) at 7.81 ppm, H-C(5) at 7.67 ppm, and Me-N(1) at 4.18 ppm, whereas N(3) correlates with H-C(2), H-C(4), and H-C(5). The correlations of the imidoyl N-atom with the *ortho*-H-atoms of Ph and the imidoyl C-atom with the *ortho*-H-atoms of 4-ClC₆H₄ are indicative of the molecular structure. The H-C group absorbing at remarkably low field (9.35/137.1 ppm) is attributed to HC(2) of the imidazolium ring. The characteristic values for the selenocyanate ion are 117.8 (^{13}C) and -129.2 ppm (^{15}N). All these chemical shifts as well as the IR absorption for the NCS⁻ ion are in very good agreement with the data of the recently studied ionic liquid 3-butyl-1-methylimidazolium selenocyanate (**16**, *Fig. 2*) [13].

*Fig. 2. Selected ^1H -, ^{13}C -, and ^{15}N -NMR shifts of **15c** in CDCl_3 (in ppm)*

A reaction mechanism for the unexpected formation of **15** is proposed in *Scheme 4*. The first step, in analogy to the reaction of 2-amino-1,3-thiazoles **10** (*Scheme 2*), may be the nucleophilic addition of imidazole **12** to the isoselenocyanate **1** to give a zwitterionic

intermediate **I**. The latter undergoes a cyclization to give the fused triazineselone derivative **L**, which then forms a new zwitterion **L** *via* ring opening. Subsequent ring closure may form the fused 1,3-diazetidone **M**, which, *via* elimination of NCSe^- , leads to the isolated imidazolium salt.

Conclusions. – The presented results extend the knowledge on reactions of amidines with imidoyl isoselenocyanates **1** to heterocycles containing an ‘amidine-like’ structure moiety. The reaction of 2-amino-1,3-thiazoles **10** parallels those with amidines and, most likely, can be extended further to similar five-membered 2-aminoheterocycles such as 2-amino-1,3-oxazoles, 2-aminoimidazoles, etc. We believe that all the reactions proceed *via* initial nucleophilic attack of the ring N-atom of the 2-aminoheterocycle at the most electrophilic heterocumulene C-atom, in contrast to the mechanism formulated for the analogous reaction with aroyl isothiocyanates [9]. On the other hand, the NH_2 group of 2-aminopyridine (**11**) is the most nucleophilic center in the reaction with **1**, leading to a selenourea derivative, which undergoes a spontaneous oxidation. Again a different type of product is formed in the reaction with 1-methylimidazole (**12**), in which the initially formed adduct cannot stabilize and, therefore, undergoes a sequence of further reactions to give the imidazolium salts.

In conclusion, isoselenocyanates **1** are prone to react with various ‘amidine-like’ molecules leading to new Se-containing heterocycles, a reaction type, which is worth to be studied further.

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Experimental Part

1. *General*. Thin layer chromatography (TLC) on silica gel 60 F₂₅₄ plates (0.25 mm, *Merck*); hexane/AcOEt 1:1 or 2:1 as eluents. Column chromatography (CC) on silica gel 60 (0.040–0.063 mm; *Merck*). Melting points (m.p.): *Büchi B-540* apparatus; in capillary, uncorrected. IR spectra: *Perkin-Elmer-Spektrum 1600 FT-IR* spectrophotometer; in KBr, in cm⁻¹. ¹H-NMR (300 or 600 MHz), ¹³C-NMR (75 or 150 MHz), and ¹⁵N-NMR (60.6 MHz) spectra: *Bruker ARX-300* or *AMX-600* instrument, in CDCl₃; chemical shifts in ppm (rel. to TMS (¹H, ¹³C) or MeNO₂ (¹⁵N)), coupling constants *J* in Hz. The multiplicities of ¹³C signals were determined with DEPT spectra. EI-MS (70 eV) and CI-MS (NH₃ as carrier gas): *Finnigan MAT-95* or *Finnigan SSQ-700* instrument; ESI-MS: *Finnigan TSQ-700*. Elemental analyses were carried out on a *Gerber Elementar Analysator EL* instrument.

2. *Starting Materials*. The preparation of *N*-phenylimidoyl isoselenocyanates **1a** – **1c** has been described in [5]. All other starting materials, **10a**, **10b**, **11**, and **12**, were commercially available (*Fluka*, *Sigma-Aldrich*) and were used without purification.

3. *Reactions of 1 with 2-Amino-1,3-thiazoles 10*. To a stirred soln. of **1** (3 – 4.5 mmol) in acetone (20 ml) at r.t. was added the equivalent amount of **10**. Immediately, a yellow to orange precipitate formed. The mixture was stirred at r.t. for 1 h, the formed precipitate was filtered under vacuum, washed with some acetone, and dried in vacuum. The products were recrystallized from acetone or DMF.

2-Phenyl-4H-1,3-thiazolo[3,2-a][1,3,5]triazine-4-selone (13a). Yield: 0.53 g (53%); from 878 mg (3.4 mmol) **1a**, 340 mg (3.4 mmol) **10a**. Orange crystals. M.p. 281.4 – 282.4° (acetone/DMF). IR (KBr): 3095*m*, 1548*m*, 1538*m*, 1513*s*, 1492*m*, 1456*s*, 1391*vs*, 1346*m*, 1325*vs*, 1296*vs*, 1279*m*, 1255*s*, 1164*w*, 1130*m*, 1093*m*, 1072*w*, 1022*w*, 999*w*, 978*w*, 942*w*, 892*m*, 848*s*, 800*w*, 756*w*, 716*s*, 693*s*. ¹H-NMR (300 MHz, CDCl₃): 8.93 (*d*, *J* = 4.9, 1 H); 8.61 – 8.57 (*m*, 2 arom. H); 7.64 – 7.57 (*m*, 1 arom. H); 7.53 – 7.48 (*m*, 2 arom. H); 7.32 (*d*, *J* = 4.9, 1 H). ¹³C-NMR (75 MHz, CDCl₃): 179.4 (*s*, C=Se); 167.5, 160.3 (2*s*, C(2), C(8a)); 133.1 (*s*, 1 arom. C); 133.6, 130.5, 128.8 (3*d*, 5 arom. CH); 128.6, 112.9 (2*d*, C(5), C(6)). EI-MS: 295 (5), 294 (3), 293 (22, *M*⁺), 291 (10), 290 (4), 289 (4), 188 (13), 187 (100), 104 (8), 103 (15), 84 (14), 77 (70). Anal. calc. for C₁₁H₇N₃SSe (292.22): C 45.21, H 2.41, N 14.38, S 10.97; found: C 45.26, H 2.40, N 14.38, S 10.96.

2-(4-Methylphenyl)-4H-1,3-thiazolo[3,2-a][1,3,5]triazine-4-selone (13b). Yield: 0.60 g (59%); from 987 mg (3.3 mmol) **1b**, 330 mg (3.3 mmol) **10a**. Yellow crystals. M.p. 295 – 296° (acetone). IR (KBr): 3131*w*, 3039*m*, 1604*w*, 1572*w*, 1536*s*, 1521*vs*, 1506*s*, 1422*s*, 1392*vs*, 1328*s*, 1300*s*, 1292*s*, 1254*s*, 1176*w*, 1166*m*, 1122*m*, 1016*w*, 892*m*, 845*s*, 790*w*, 772*m*, 740*s*, 711*w*. CI-MS: 310 (20), 309 (13), 308 (100, [*M*+1]⁺), 307 (8), 306 (48), 305 (16), 304 (16). Anal. calc. for C₁₂H₉N₃SSe (306.25): C 47.06, H 2.96, N 13.72, S 10.47; found: C 47.04, H 3.07, N 13.63, S 10.46.

2-(4-Chlorophenyl)-4H-1,3-thiazolo[3,2-a][1,3,5]triazine-4-selone (13c). Yield: 0.59 g (58%); from 991 mg (3.1 mmol) **1c**, 310 mg (3.1 mmol) **10a**. Yellow crystals. M.p. 280° (dec., acetone). ¹H-NMR (300 MHz, CDCl₃): 8.92 (*d*, *J* = 4.9, 1 H); 8.53, 7.47 (*AA'**BB'*, *J*_{AB} = 8.9, 4 arom. H); 7.31 (*d*, *J* = 4.9, 1 H). ¹³C-NMR (75 MHz, CDCl₃): 179.4 (*s*, C=Se); 167.6, 159.3 (2*s*, C(2), C(8a)); 140.2, 130.5 (2*s*, 2 arom. C); 131.7, 129.1 (2*d*, 4 arom. CH); 128.6, 113.0 (2*d*, C(5), C(6)). Anal. calc. for C₁₁H₆ClN₃SSe (326.67): C 40.45, H 1.85, N 12.86, S 9.82; found: C 40.26, H 2.04, N 12.83, S 9.96.

7-Methyl-2-phenyl-4H-1,3-thiazolo[3,2-a][1,3,5]triazine-4-selone (13d). Yield: 0.60 g (58%); from 878 mg (3.4 mmol) **1a**, 388 mg (3.4 mmol) **10b**. Orange crystals. M.p. 280 – 281° (acetone/DMF). IR (KBr): 3101_w, 3053_w, 3031_w, 2967_w, 1587_m, 1518_{vs}, 1492_m, 1456_s, 1401_{vs}, 1384_{vs}, 1341_s, 1326_s, 1298_m, 1273_m, 1256_s, 1182_m, 1137_m, 1100_m, 1080_m, 1021_w, 996_w, 941_w, 879_m, 838_s, 807_m, 743_s, 693_m. ¹H-NMR (300 MHz, CDCl₃): 8.66 (*q*-like, *J* = 1.4, 1 H); 8.56 – 8.54 (*m*, 2 arom. H); 7.62 – 7.51 (*m*, 1 arom. H); 7.49 – 7.46 (*m*, 2 arom. H); 2.53 (*d*, *J* = 1.4, Me). ¹³C-NMR (75 MHz, CDCl₃): 178.7 (*s*, C=Se); 167.1, 160.0 (2*s*, C(2), C(8a)); 133.9, 127.1 (2*s*, 1 arom. C, C(7)); 133.4, 130.4, 128.7 (3*d*, 5 arom. CH); 126.8 (*d*, C(6)); 13.5 (*q*, Me). EI-MS: 309 (12), 308 (8), 307 (55, *M*⁺), 305 (27), 304 (10), 303 (9), 202 (13), 201 (100), 198 (15), 197 (14). Anal. calc. for C₁₂H₉N₃SSe (306.25): C 47.06, H 2.96, N 13.72, S 10.47; found: C 46.99, H 2.83, N 13.85, S 10.63.

7-Methyl-2-(4-methylphenyl)-4H-1,3-thiazolo[3,2-a][1,3,5]triazine-4-selone (13e). Yield: 0.93 g (63%); from 1.376 g (4.6 mmol) **1b**, 524 mg (4.6 mmol) **10b**. Orange-yellow crystals. M.p. 291° (dec., DMF). IR (KBr): 3074_m, 2933_w, 1606_w, 1589_m, 1573_w, 1530_{vs}, 1508_s, 1456_m, 1420_s, 1393_{vs}, 1359_s, 1333_s, 1298_s, 1275_s, 1257_s, 1179_m, 1140_s, 1111_m, 1100_m, 1018_w, 992_w, 877_m, 848_s, 852_w, 836_s, 764_s. CI-MS: 324 (21), 323 (15), 322 (100, [*M*+1]⁺), 321 (8), 320 (49), 319 (17), 318 (17), 258 (7). Anal. calc. for C₁₃H₁₁N₃SSe (320.28): C 48.75, H 3.46, N 13.12, S 10.01; found: C 48.58, H 3.37, N 13.07, S 10.11.

7-Methyl-2-(4-chlorophenyl)-4H-1,3-thiazolo[3,2-a][1,3,5]triazine-4-selone (13f). Yield: 0.65 g (62%); from 991 mg (3.1 mmol) **1c**, 353 mg (3.1 mmol) **10b**. Orange crystals. M.p. 282.0 – 282.5° (DMF). ¹H-NMR (300 MHz, CDCl₃): 8.65 (*q*-like, *J* = 1.4, 1 H); 8.50, 7.46 (*AA'**BB'*, *J*_{AB} = 8.7, 4 arom. H); 2.54 (*d*, *J* = 1.4, Me). ¹³C-NMR (75 MHz, CDCl₃): 179.0 (*s*, C=Se); 168.0, 158.0 (2*s*, C(2), C(8a)); 140.2, 132.2, 127.5 (3*s*, 2 arom. C, C(7)); 131.5, 129.0 (2*d*, 4 arom. CH); 126.7 (*d*, C(6)); 13.4 (*q*, Me). EI-MS: 343 (17), 342 (6), 341 (38, *M*⁺), 340 (5), 339 (17), 338 (6), 337 (6), 268 (23), 253 (45), 237 (37), 236 (12), 235

(100). Anal. calc. for $C_{12}H_8ClN_3SSe$ (340.69): C 42.31, H 2.37, N 12.33, S 9.41; found: C 42.10, H 2.29, N 12.26, S 9.27.

4. *Reaction of 1c with 2-Amino-3-methylpyridine (11)*. To a stirred soln. of **1c** (992 mg, 3.1 mmol) in acetone (20 ml) at r.t., one equivalent of **11** (335 mg, 3.1 mmol) was added, and the mixture was stirred for 3 h, until the starting materials were completely consumed (TLC). Then, the mixture was poured into H_2O and stirred for another 1 h. The yellowish precipitate was filtered under vacuum and recrystallized from Et_2O to give 0.85 g (64%) of 2-(4-chlorophenyl)-9-methyl-3-phenyl-3H-4 λ^4 -[1,2,4]selenadiazolo[1',5':1,5][1,2,4]selenadiazolo[2,3-a]pyridine (**14**). M.p. 189.5 – 190.5. IR: 3041 w , 2955 w , 2948 w , 1605 w , 1592 w , 1567 w , 1511 s , 1463 s , 1445 m , 1401 s , 1367 vs , 1319 m , 1300 m , 1286 s , 1274 s , 1223 m , 1196 s , 1125 m , 1104 m , 1089 m , 1071 w , 1015 m , 992 w , 951 m , 892 w , 838 m , 778 m , 765 w , 748 m , 734 m . 1H -NMR (300 MHz, $CDCl_3$): 8.24 (*dd*-like, $J = 8.7, 0.8, 1$ H); 7.63 – 7.54 (*m*, 3 H); 7.35 – 7.20 (*m*, 5 H); 7.08 – 7.04 (*m*, 2 H); 6.84 (*dd*-like, $J = 7.0, 5.8, 1$ H); 2.64 (*s*, Me). ^{13}C -NMR (75 MHz, $CDCl_3$): 174.4 (*s*, C=Se); 162.2, 156.4, 141.2, 136.2, 131.0, 130.5 (6 s , 3 arom. C, 3 C); 137.0, 135.0, 126.2, 115.4 (4 d , 1 arom. CH, 3 CH); 131.5, 129.3, 128.1, 125.5 (4 d , 8 arom. CH); 17.5 (*q*, Me). CI-MS: 430 (5), 429 (38), 428 (19), 427 (100, $[M+1]^+$), 426 (13), 425 (46), 424 (15), 423 (15), 349 (14), 347 (25), 233 (13), 231 (41), 136 (7), 134 (12). Anal. calc. for $C_{20}H_{15}ClN_4Se$ (425.78): C 56.42, H 3.55, N 13.16, Cl 8.33; found: C 56.00, H 3.66, N 12.97, Cl 8.50.

Suitable crystals for the X-ray crystal-structure determination were obtained from Et_2O /AcOEt.

5. *Reactions of 1 with 3-Methylimidazole (12)*. To a soln. of **1b** (987 mg, 3.3 mmol) or **1c** (895 mg, 2.8 mmol) in acetone (30 ml), one equivalent of **12** (271 mg and 230 mg, resp.) was added, and the mixture was stirred at r.t. overnight. TLC indicated that the starting materials were completely consumed. Then, the mixture was poured into ice/ H_2O and stirred

for another 2 h. The yellowish precipitate was filtered under vacuum and recrystallized from AcOEt.

1-Methyl-3-(N-phenyl-4-methylbenzimidoyl)imidazolium selenocyanate (15b): Yield: 0.66 g (52%). Pale yellow crystals. M.p. 116.5 – 117.5° (AcOEt). IR: 3181_w, 3083_m, 2061_{vs}, 1654_s, 1608_m, 1583_s, 1537_s, 1509_w, 1484_m, 1449_w, 1417_m, 1333_s, 1272_m, 1233_s, 1211_m, 1189_m, 1143_s, 1088_m, 1023_w, 927_s, 907_w, 831_m, 794_w, 766_m, 727_m, 695_s. ¹H-NMR (600 MHz, CDCl₃): 9.30 (br. *s*, H–C(2)(imid)); 7.78 – 7.76, 7.74 – 7.72 (2_{*m*}, 2 H(imid)); 7.33 – 7.27 (*m*, 2 arom. H); 7.27 – 7.15 (*m*, 4 arom. H); 7.12 – 7.02 (*m*, 1 arom. H); 6.84 – 6.78 (*m*, 2 arom. H); 4.19 (*s*, MeN); 2.36 (*s*, Me). ¹³C-NMR (150 MHz, CDCl₃): 148.7 (*s*, C=N); 145.2, 142.8, 123.8 (3_{*s*}, 3 arom. C); 136.9 (*d*, C(2)H(imid)); 130.2, 129.6, 129.0, 121.2 (4_{*d*}, 2 arom. CH each); 125.5 (*d*, 1 arom. CH); 124.5, 119.8 (2_{*d*}, 2 CH(imid)); 117.6 (*s*, NCSe); 37.7 (*q* MeN); 21.5 (*q*, Me). ¹⁵N-NMR (60.6 MHz, CDCl₃): –205.3 (N(1)); –178.3 (N(3)); –78.6 (C=N)³). Anal. calc. for C₁₉H₁₈N₄Se (381.34): C 59.84, H 4.76, N 14.69; found: C 59.71, H 4.76, N 14.61.

1-Methyl-3-(N-phenyl-4-chlorobenzimidoyl)imidazolium selenocyanate (15c): Yield: 0.62 g (55%). Pale yellow crystals. M.p. 144° (dec., AcOEt). IR: 3140_m, 3071_s, 2060_{vs}, 1672_{vs}, 1594_s, 1532_s, 1489_s, 1449_w, 1415_m, 1402_m, 1359_m, 1332_m, 1274_m, 1256_s, 1214_w, 1180_w, 1142_s, 1110_m, 1089_s, 1015_m, 927_s, 904_w, 838_m, 778_w, 765_m, 741_s, 699_s. ¹H-NMR (600 MHz, CDCl₃): 9.34 (br. *s*, H–C(2)(imid)); 7.82 – 7.80, 7.68 – 7.60 (2_{*m*}, 2 H(imid)); 7.48 – 7.39 (*m*, 4 arom. H); 7.28 – 7.20 (*m*, 2 arom. H); 7.11 – 7.06 (*m*, 1 arom. H); 6.83 – 6.79 (*m*, 2 arom. H); 4.17 (*s*, MeN). ¹³C-NMR (150 MHz, CDCl₃): 147.6 (*s*, C=N); 144.8, 138.4, 125.2 (3_{*s*}, 3 arom. C); 137.1 (*d*, C(2)H(imid)); 131.3, 129.8, 129.1, 121.1 (4_{*d*}, 2 arom. CH each); 125.7 (*d*, 1 arom. CH); 124.5, 119.7 (2_{*d*}, 2 CH(imid)); 117.6 (*s*, NCSe); 37.7 (*q* MeN). ¹⁵N-NMR (60.6 MHz, CDCl₃): –202.4 (N(1)); –177.1 (N(3)); –129.2 (NCSe); –72.9 (C=N). Anal.

³) The signal for NCSe[–] could not be detected.

calc. for $C_{18}H_{15}ClN_4Se$ (401.76): C 53.81, H 3.76, Cl 8.82, N 13.95; found: C 53.71, H 3.79, Cl 8.94, N 13.82.7.

X-Ray Crystal-Structure Determination of 14 (Table and Fig. 1)⁴). All measurements were performed on a *Rigaku AFC5R* diffractometer using graphite-monochromated MoK_{α} radiation (λ 0.71073 Å) and a 12kW rotating anode generator. The data collection and refinement parameters are given in the Table, and a view of the molecule is shown in the Figure. The intensities were corrected for *Lorentz* and polarization effects. An empirical absorption correction based on azimuthal scans of several reflections [14] was applied. The structure was solved by direct methods using SIR92 [15], which revealed the positions of all non-H-atoms. The non-H-atoms were refined anisotropically. The H-atoms were placed in geometrically calculated positions and refined using a rigid model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent atom. Refinement of the structure was carried out on F^2 using full-matrix least-squares procedures, which minimized the function $\sum w(F_o^2 - F_c^2)^2$. A correction for secondary extinction was not applied. Neutral atom scattering factors for non-H-atoms were taken from [16a], and the scattering factors for H-atoms were taken from [17]. Anomalous dispersion effects were included in F_c [18]; the values for f' and f'' were those of [16b]. The values of the mass attenuation coefficients are those of [16c]. All calculations were performed using the SHELXL97 program [19].

Table 2. *Crystallographic Data for Compound 14*

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⁴) CCDC-827538 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre* via http://www.ccdc.cam.ac.uk/data_request/cif.

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Legends

Fig. 1. *ORTEP Plot* [10] of the molecular structure of **14** (50% probability ellipsoids, arbitrary numbering of the atoms)

Fig. 2. *Selected ^1H -, ^{13}C -, and ^{15}N -NMR shifts of **15c** in CDCl_3 (in ppm)*

Table 1. Prepared 2-Aryl-4H-1,3-thiazolo[3,2-a][1,3,5]triazole-4-selones **13**

1	10	13	Yield (%)
a Ar = Ph	a R = H	a Ar = Ph, R = H	53
b Ar = 4-MeC ₆ H ₄	a R = H	b Ar = 4-MeC ₆ H ₄ , R = H	60
c Ar = 4-ClC ₆ H ₄	a R = H	c Ar = 4-ClC ₆ H ₄ , R = H	60
a Ar = Ph	b R = Me	d Ar = Ph, R = Me	57
b Ar = 4-MeC ₆ H ₄	b R = Me	e Ar = 4-MeC ₆ H ₄ , R = Me	63
c Ar = 4-ClC ₆ H ₄	b R = Me	f Ar = 4-ClC ₆ H ₄ , R = Me	63

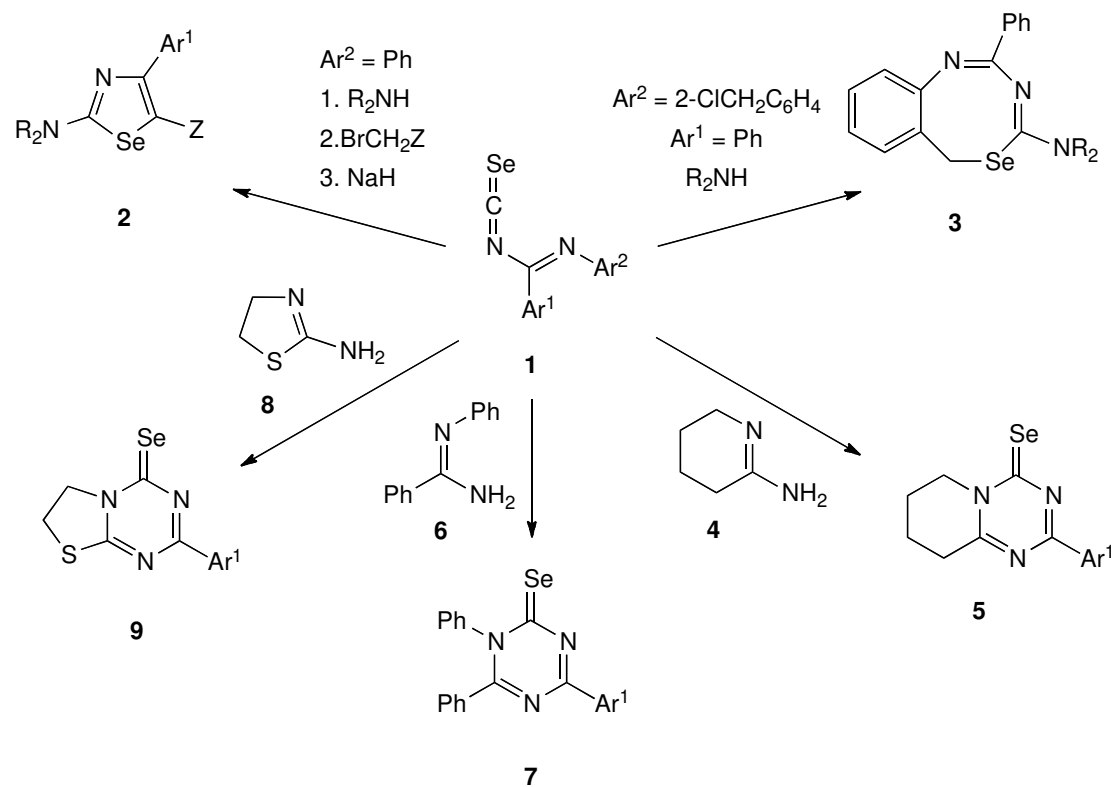
Table 2. Crystallographic Data for Compound **14**

Crystallized from	Et ₂ O/AcOEt
Empirical formula	C ₂₀ H ₁₅ ClN ₄ Se
Formula weight	425.72
Crystal color, habit	yellow, prism
Crystal dimensions [mm]	0.30 × 0.35 × 0.45
Temperature [K]	173(1)
Crystal system	triclinic
Space group	P^{-}_1
<i>Z</i>	2
Reflections for cell determination	25
2 θ range for cell determination [°]	39 – 40
Unit cell parameters <i>a</i> [Å]	9.021(1)
<i>b</i> [Å]	9.503(1)
<i>c</i> [Å]	10.849(2)
α [°]	86.66(1)
β [°]	76.76(1)
γ [°]	89.33(1)
<i>V</i> [Å ³]	903.7(3)

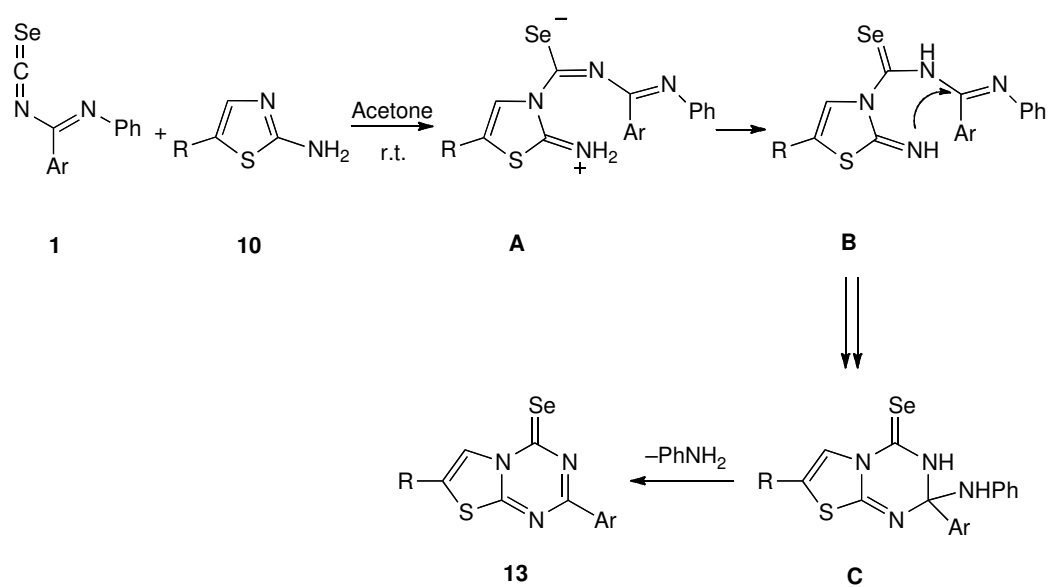
D_x [g cm ⁻¹]	1.564
$\mu(\text{MoK}\alpha)$ [mm ⁻¹]	2.235
Scan type	$\omega/2\theta$
$2\theta(\text{max})$ [°]	60
Transmission factors (min; max)	0.867; 1.000
Total reflections measured	5584
Symmetry independent reflections	5290
Reflections with $I > 2\sigma(I)$	4284
Parameters refined	236
Final $R(F)$ [$I > 2\sigma(I)$ reflections]	0.0362
$wR(F^2)$ (all data)	0.0973
Weighting parameters: a, b^a)	0.053, 0.1553
Goodness of fit	1.056
Final $\Delta_{\text{max}}/\sigma$	0.003
$\Delta\rho$ (max; min) [e Å ⁻³]	0.84; -0.79

^{a)} $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$

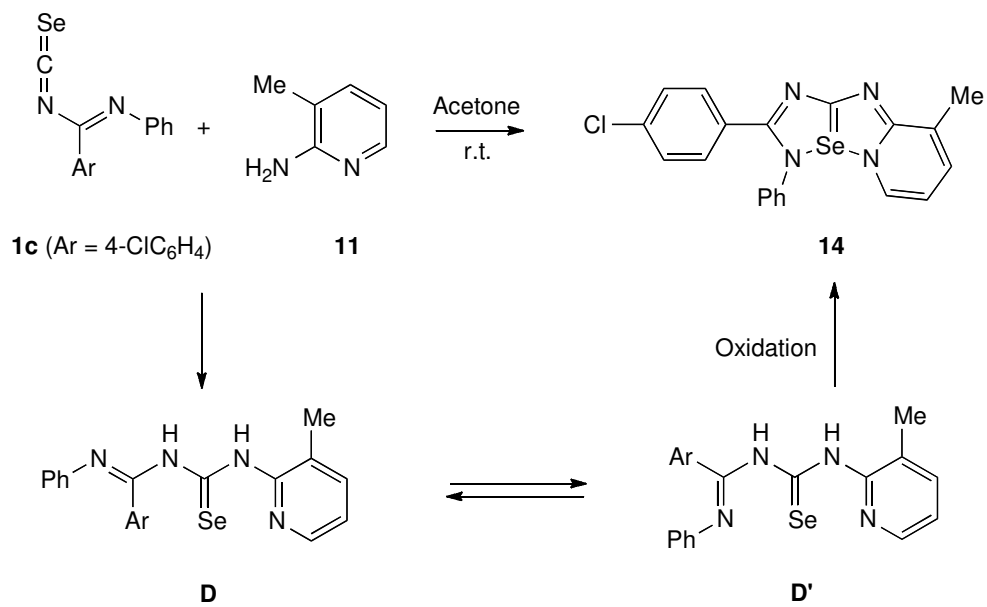
Scheme 1



Scheme 2



Scheme 3



Scheme 4

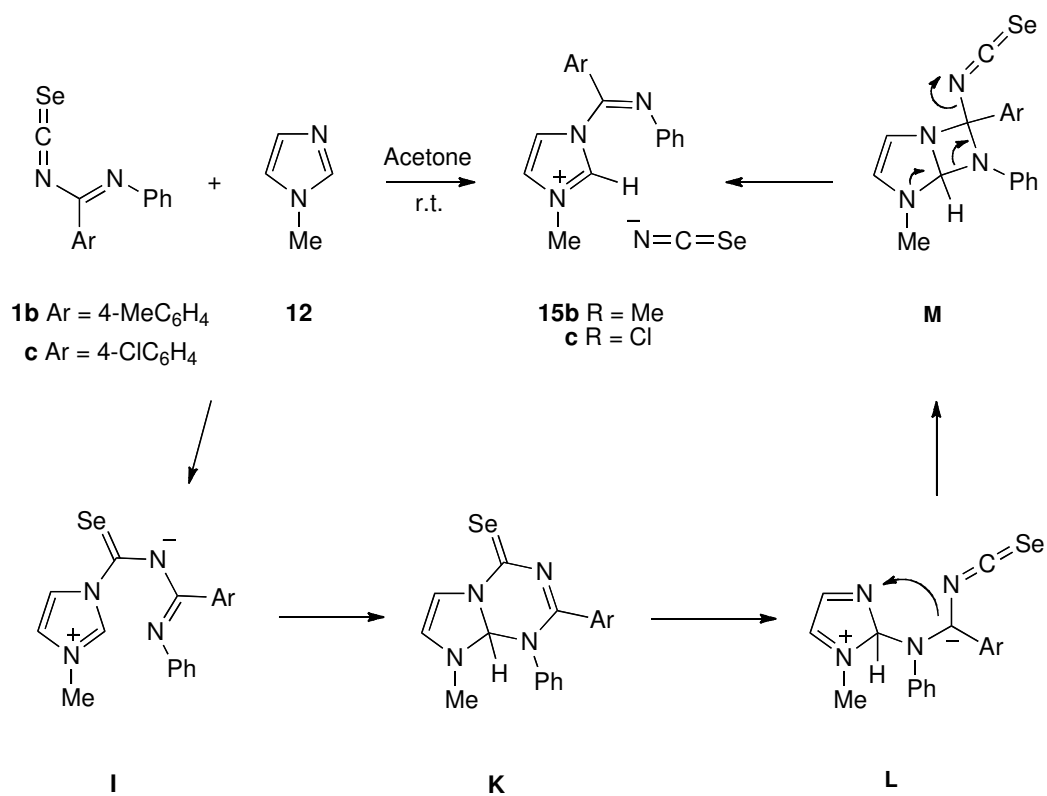


Figure 1

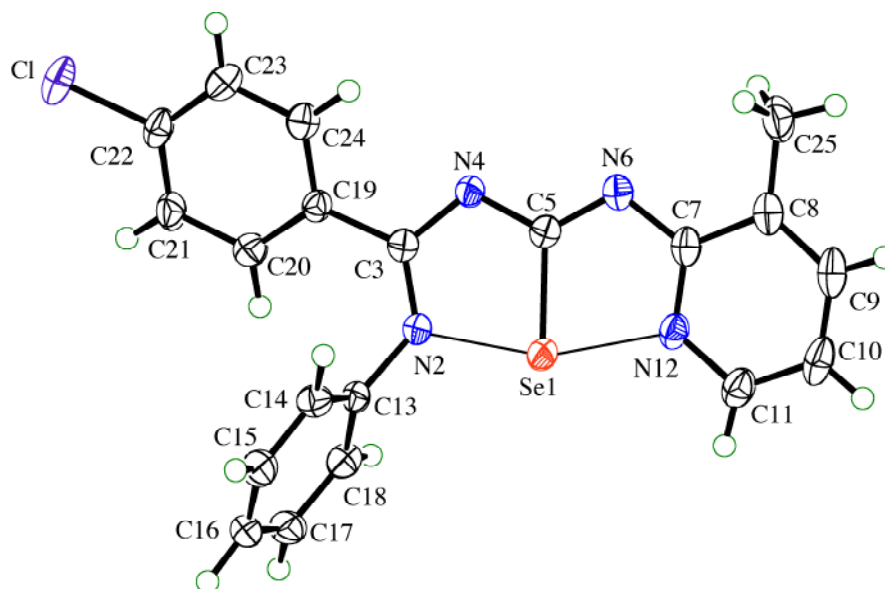
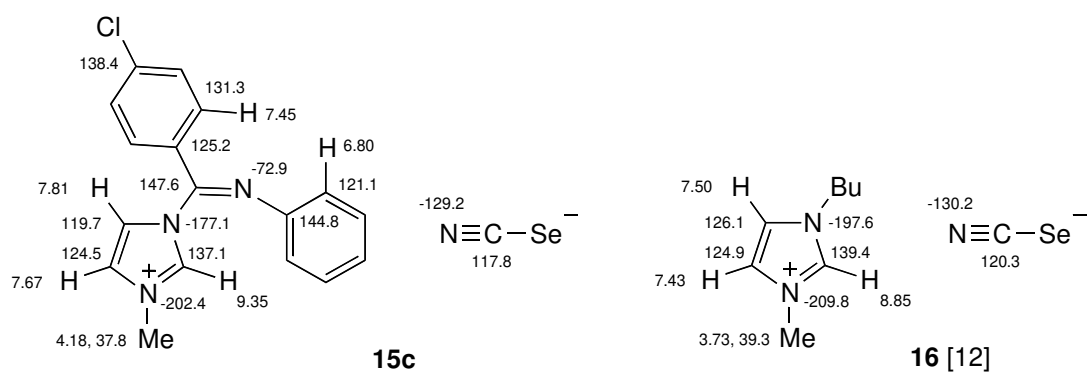


Figure 2



Graphical Abstract